

# Effect of Hydrogen Pressure on Rate of Direct Coal Liquefaction

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## Introduction

There have been numbers of studies for direct coal liquefaction. Many of them have been carried out with batch autoclaves, which are heated up to a designed temperature (hereinafter called nominal reaction temperature), followed by holding at that temperature for a desired time (hereinafter called nominal reaction time) and cooling down. Then total pressure inside the autoclaves changes with the temperature varying and consuming of hydrogen by the reaction. Thus the hydrogenation of coal is non-isothermal and non-isobaric. Workers, however, have analysed kinetics conventionally considering experimental results by the autoclave as those under isothermal and isobaric conditions at a reaction time according to a nominal reaction time (NRT) (1-6)

The authors pointed out that the conventional analysis (hereinafter called isothermal analysis) was unsuitable for not only investigation of reaction kinetics represented by a scheme including a unobservable species but also calculation of the real value of rate parameters (7). Effect of hydrogen pressure on a rate of the reaction has been investigated by some workers (1-3). They examined dependence of initial hydrogen pressure or average pressure during period of NRT on rate constants which are calculated by the isothermal analysis using data obtained under different initial pressures at same nominal reaction temperature (NRTM). From the same reason as above mentioned, however, it may be doubtful for these studies to be calculated a accurate value of rate parameters.

In this report, hydrogen pressure effect on the rate and rate parameters values was estimated by non-isothermal analysis, in which experimental results with a batch autoclave were allowed to remain non-isothermal and non-isobaric.

## Apparatus and Procedure

The experiments were carried out with a shaking type 0.5-liter autoclave. The apparatus and procedure were identical with those previously described (7). Experiments were made under the following conditions: from 350°C to 440°C NRTM, from 2-minutes to about 2-hours NRT and from 50 atm to 110 atm initial hydrogen pressure. 12 grms of powdered coal and 28 grms hydrogenated and recrystallized anthracene oil as vehicle were used. A catalyst, consisting powdered sulphur, ferrihydride and molybdenic oxide in 1:1:1 at weight ratio, was prepared in this laboratory. Taiheiyo coal (Japanese) and Morwell coal (Australian) were studied. Ultimate analysis, on a moisture-free basis, showed that Taiheiyo coal had a higher carbon-to-hydrogen ratio of 1.17 (79.8%C and 5.7%H) than that of 1.05 (65.3%C and 5.2%H) in

Morwell coal. Proximate analysis showed that moisture, fixed carbon and volatile materials contents (%) were 12.6, 52.4 and 34.2 for Morwell coal, and being 4.9, 27.7 and 47.0% for Taiheiyo coal, respectively.

Extents of reaction were determined by measuring product solubility in two solvents, benzene and n-hexane. Then organic benzene insolubles (OBIS), in which unconverted coal and cokes produced by side reactions were contained, asphaltene and oil were separated and weighed by the general procedure (6)

#### Experimental Results and Discussions

Examples of process time-temperature and process time-pressure curves, at different NRT's, are given in Fig. 1. The changes in pressure indicates that the absorption of hydrogen apparently is initiated about 250°C, and after the temperature has been reached at the NRTM of 440°C, the pressure begins to decrease at almost constant rate by consuming of hydrogen with the hydrogenation, follows by rapid decreasing as the temperature decreases. Fig. 2 and 3 represent the experimental results of Morwell coal liquefaction under various initial hydrogen pressures at 350°C of NRTM. Those represent that dependence of reaction course and the rate on the initial hydrogen pressure is not very sharp: under any pressure the courses show similar trends—i.e., an increased NRT increases oil formation from coal, while it has less influence on asphaltene production. Compared with the reaction extent at zero NRT (that during pre-heating and quenching period), the extent for NRT period is little. Liquefaction, moreover, progresses to fair degree in spite of low NRTM of 350°C. These hydrogenation characteristics may be explained from Morwell coal's properties: pyrolysis accompanying deoxygenation from groups containing oxygene will precedes hydrogenation, because Morwell coal have much oxygene contents of 30% (by difference) as indicated from the ultimate analysis; this coal is converted into oil and asphaltene to appreciable degree by the pyrolysis through the pre-heating and quenching period, and remaining unreacted coal is reacted to form oil. Fig. 4 and 5 show the experimental results for Taiheiyo coal. From those it is found that there is a tendency to increase reaction rate with increasing initial hydrogen pressure, and being a marked one at the higher NRTM; moreover, the higher initial hydrogen pressure prevents cokes formation from occurring: under the lowest initial hydrogen pressure at NRTM of 440°C, oil yield decreases against OBIS fraction increasing with increasing NRT. This can be expressed as produced oil is degraded to make cokes, which is measured as OBIS. On the other hand, under higher initial hydrogen pressures there is little influence of oil degradation.

#### Hydrogenation Rate Analysis

From previously reported facts (1-6) it may be considered that coal is liquefied through the following two-step process as the main reaction, coal → asphaltene → oil. Then under severe reaction conditions of higher temperature, or under the influence of a active catalyst, gasification and cokes formation is accompanied with the main reaction simultaneously. For a case where the oil is degraded to an appreciable degree, the authors proposed the following four-step scheme taking into account cokes formation from polymerization of the oil, coal → asphaltene → oil → resin → cokes (7). With this scheme Miike coal (Japanese) liquefaction behaviors were investigated using

the non-isothermal analysis method to be well expressed. To describe the Morwell coal liquefaction properties, however, the above mentioned scheme must be modified by addition of another reaction process such as one step oil formation, coal→oil. Therefore, in this study a reaction scheme was derived so as to express the experimental hydrogenolysis courses, and its kinetic parameters values including reaction order with respect to hydrogen pressure were estimated so that simulated courses might have close agreement with the experimental ones. On estimation of the rate parameters values in the derived reaction scheme, as its rate equations was so complicated that an analytical method might be unsuitable, a numerical analysis based on the non-linear least sum of squares method was used; Marquardt method was adopted because of its good convergency. A estimation procedure is illustrated with flow chart. Its detail is as follows: experimental reaction temperatures and pressures values at ten or fifteen process times in each run were stored up; from these storage reaction temperature and pressure-process time curves of each run were described by a spline function (9); reaction courses of each run were simulated using the rate equations; from this function and values of rate parameters, i.e., reaction orders, activation energies and frequency factors, the parameters values were optimally estimated from comparing the simulated courses with experimental ones. To remove interference with the optimum estimation by compensation effect between frequency factor and activation energy, variables were transformed (10). A detail of investigated results will be presented in the meeting.

## Conclusions

Effect of hydrogen pressure on coal hydrogenation properties was investigated. It was found that for liquefaction of Morwell coal in which oxygen contents appears to be considerable, hydrogen pressure little effect. In the case of Taiheiyo coal liquefaction hydrogen pressure had effects: higher pressure gave higher oil yield and prevented cokes formation from occurring.

A reaction scheme was derived so as to express the experimental liquefaction courses, and kinetics was analysed by the proposed non-isothermal method using the batch autoclave data which is non-isothermal and non-isobaric ones.

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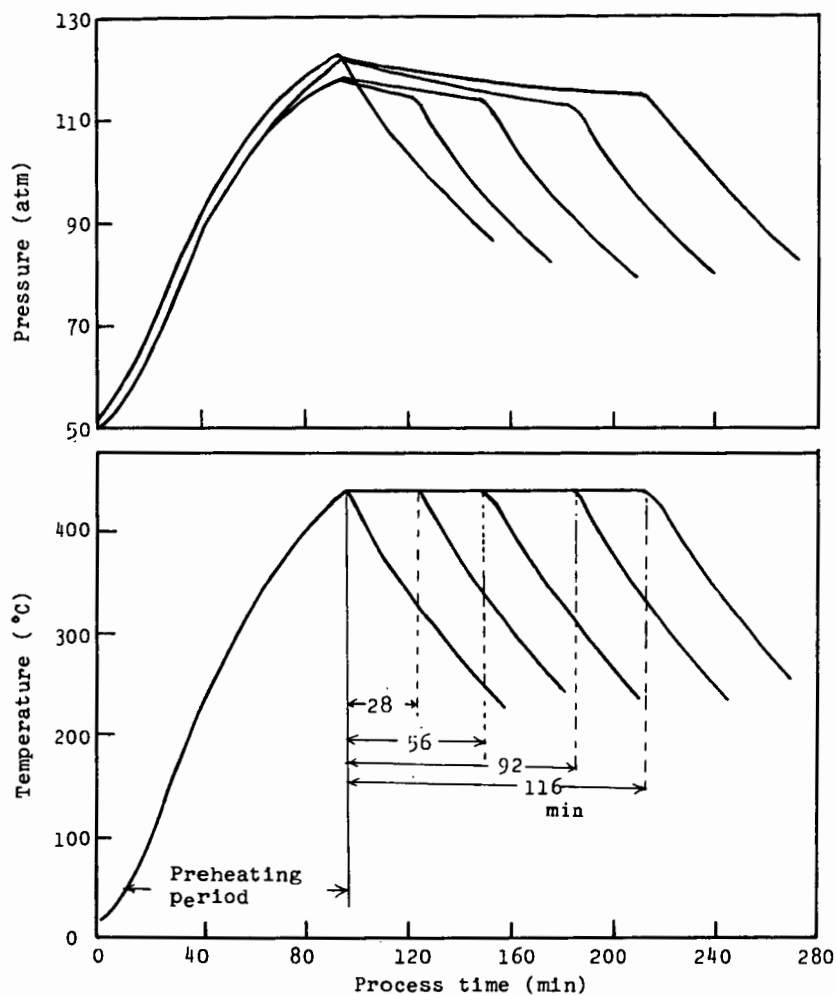


Fig. 1 Examples of the experimental pressure- and temperature-  
curves at the nominal reaction temperature (NRT) of  
440 °C under several nominal reaction times (NRT)

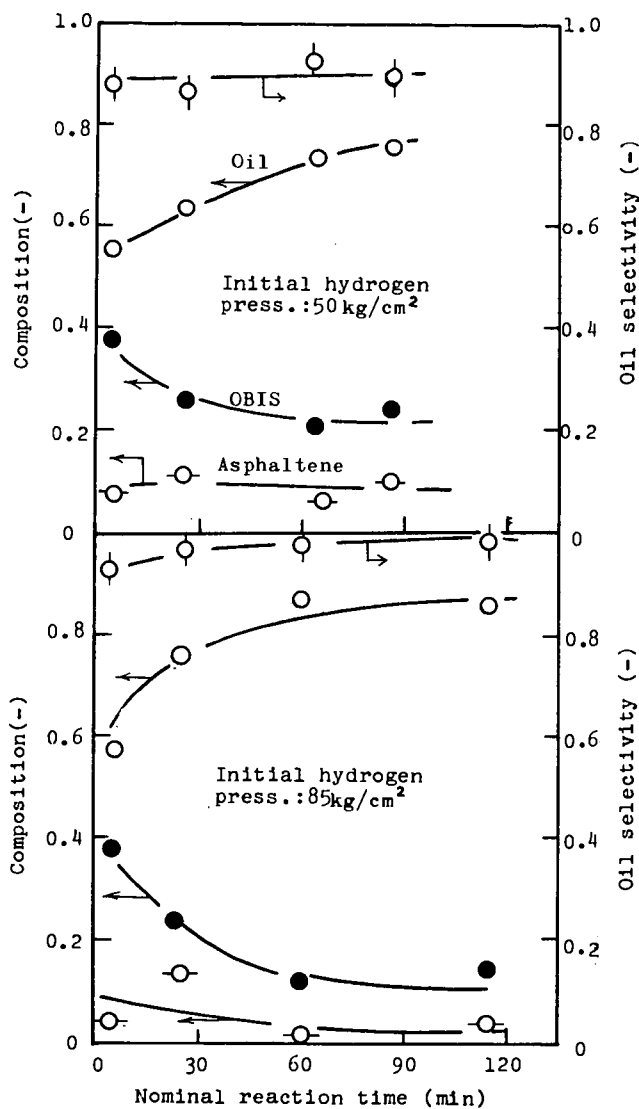


Fig. 2 Liquefaction course of Morwell coal under lower initial hydrogen pressure at NRTM of 350°C

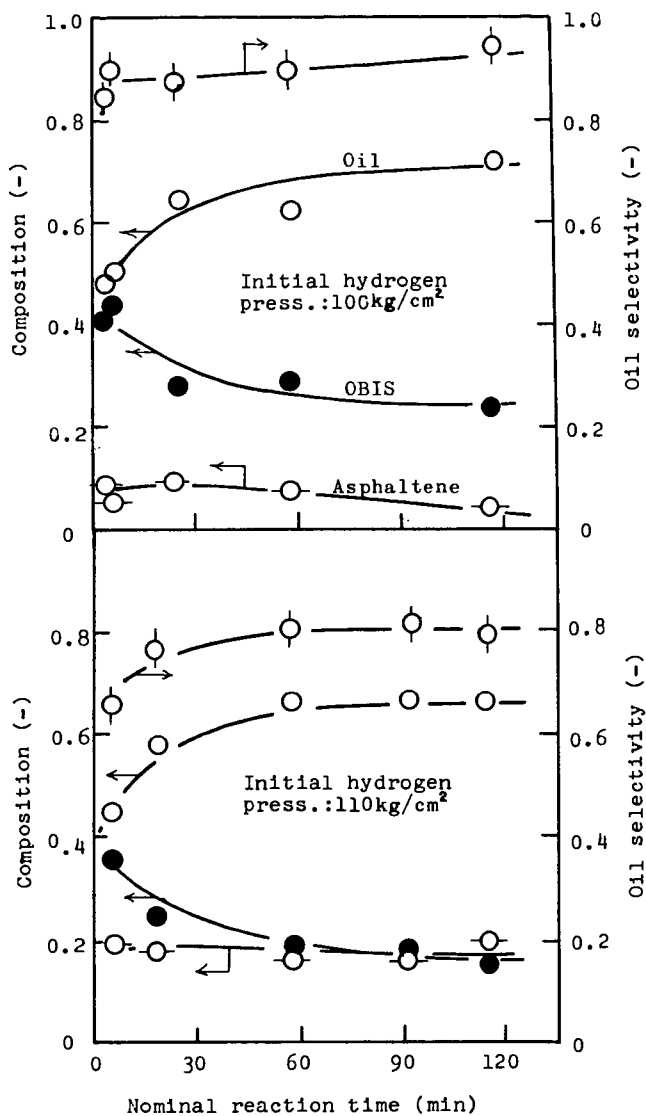


Fig. 3 Liquefaction course of Morwell coal under higher initial hydrogen pressure at NRTM of 350°C

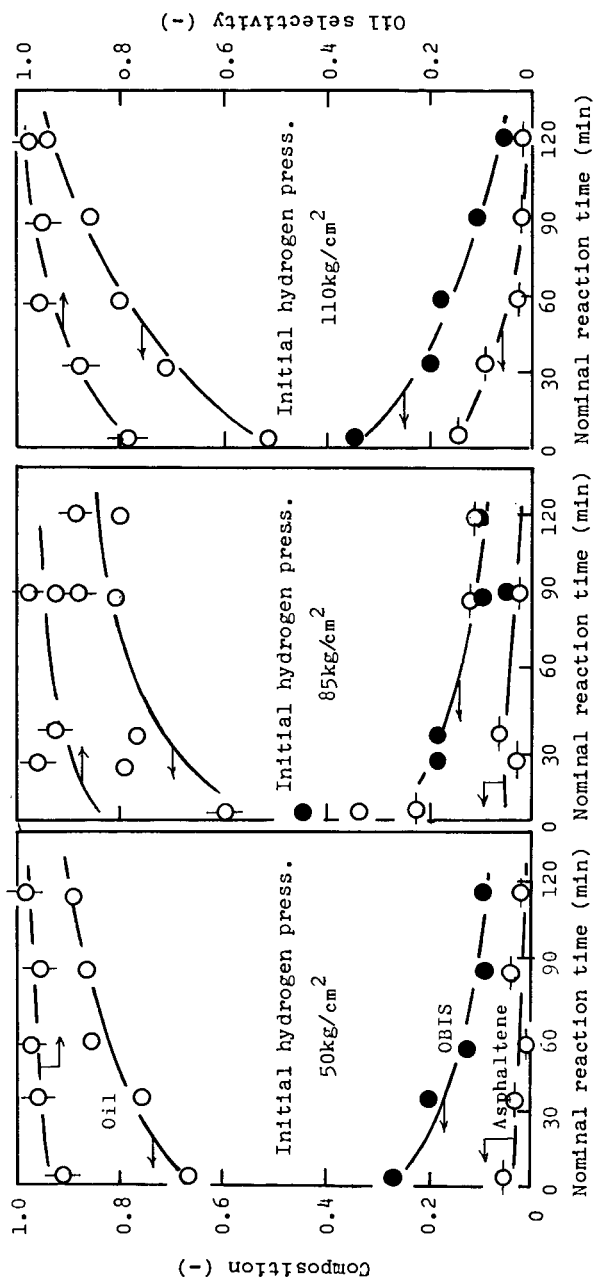


Fig. 4 Dependence of initial hydrogen pressure on liquefaction course of Taiheiyō coal at lower NRTM of 380°C



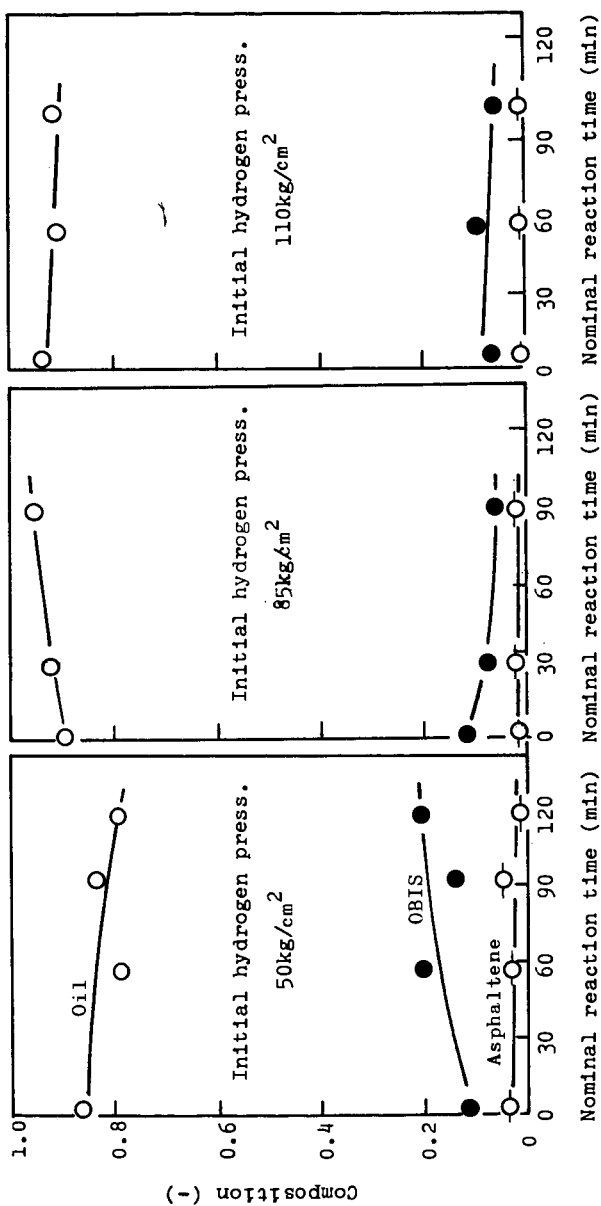


Fig. 5 Dependency of initial hydrogen pressure on liquefaction course of Taiheiyo coal at higher NRTM of 440°C

# Flow chart

